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Nanomaterials for alternative energy sources

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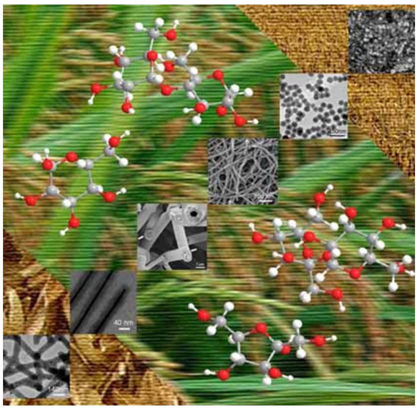

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Inorganic nanomaterials for batteries

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The availability of inorganic materials at the nano-dimension opens up opportunities for advanced battery designs and architectures. This Perspective focuses on the opportunities for nanomaterials in all elements of batteries, describing where they might find application and also discussing their limitations. We concentrate on alloys and oxides for the anode, on the olivine phosphate for the cathode and the formation of the interphases between them and its dependence on the electrolyte in lithium batteries.

Introduction

There has been a large increase in the use and demand for rechargeable batteries with higher energy densities for use in mobile electronic devices that are demanding higher power capabilities. As a result, lithium based systems have begun to dominate the consumer market place, at the expense of nickel metal hydride and the toxic nickel cadmium systems. However, in their efforts to increase the storage capacities within a constrained physical environment, some manufacturers have pushed the limit too far with resulting electrical shortages and failures, in some cases fires.

By their very nature, chemical energy storage systems such as batteries are inherently metastable, and the goal is to harness the available energy in an electrochemical process rather than in chemical side-reactions. The goal of the chemist is to design a process that is selective to the desired reaction. Thus, most successful batteries are based on intercalation reactions, which are kinetically favored over reactions involving structural change, which need to nucleate a new phase. Thus, in the classical dry cell hydrogen ions are inserted into the manganese dioxide lattice forming manganese oxyhydroxide, MnOOH. In a typical intercalation reaction, the hydrogen or lithium is intercalated into the structural lattice without major changes occurring to the lattice, except for slight lattice expansions or contractions.

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To minimize side-reactions with for example the electrolyte, the cell container or current collectors, it is common to reduce the bulk reactivity of the material. Thus, in the titanium disulfide cells a slight excess of titanium, around 0.5 to 1%, was incorporated into the structure. This reduced the thermodynamic activity of the sulfur, and hence its corrosivity significantly, without noticeably reducing the rate of intercalation of the lithium. SONY in its commercial $LiCoO_2$ cells, intentionally adds excess lithium in the manufacturing process so that the $LiCoO_2$ sinters to 15 to 20 micron size particles thus reducing its reactivity with the electrolyte and increasing the cell's safety.[1]

To fulfill the need for high power electrochemical cells, there is a need to go to higher surface area materials which should inherently have a higher reaction rate. The natural step is to look at nanomaterials with their surface areas in excess of 5 $m^2 g^{-1}$ and often up to several hundred $m^2 g^{-1}$. However, as noted above, this increase of surface area will also increase the side-reactions and potentially reduce the safety of the cells. Thus, the chemist must be very careful in selecting which materials can be used at the nano-size—the materials must inherently be very stable, that is have a high activation energy toward side-reactions. Thus, materials such as $LiNiO_2$ which on charging forms the very unstable NiO_2 with an oxygen activity likely above one atmosphere are not viable candidates. On the other hand, a material such as $LiFePO_4$, where all the oxygen is bound-up in the very stable phosphate, PO_4, group is a possible candidate. In addition to the physical effect of increased surface area, there is also the possibility of change of physical and chemical behavior as the particles become sufficiently small.

In this Perspective, we will discuss some opportunities and challenges for nanomaterials in several components of electrochemical cells for energy storage. A schematic of a typical cell is shown in Fig. 1. Included in this Perspective will be a discussion of the anode, long dominated by carbon intercalation electrodes, the nanostructured solid electrolyte interphase (SEI) layer that coats the anode and cathode making them stable to the electrolyte, and the cathode. In addition, some discussion will center on the addition of electrically conductive nanoparticles that can enhance the electronic conductivity, for example carbon nanotubes with their extreme aspect ratios. The electrolyte also plays a key role in the nanoscience of batteries, as it is the source of the chemical

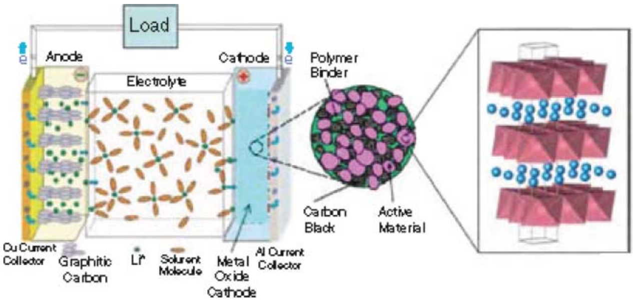

Fig. 1 Schematic of a battery showing the critical components that might be impacted by nano materials. Reprinted with permission from M. S. Whittingham, *MRS Bull.*, 2008, **33**, 411–420. Copyright 2008 Materials Research Society.

species needed to form the hybrid inorganic/organic SEI layer, and also must be able to effectively wet the electrode materials. A major challenge to the inorganic chemist is how to characterize the structure and bonding in these nanomaterials, which can be amorphous, and in which the atoms move around as the lithium ions are inserted or removed on cell discharge or charge.

Anodes

The anode of lithium cells has been dominated by carbons, which can intercalate lithium reversibly. Carbon can form the compound LiC_6, which has storage capabilities of 340 A h kg^{-1} and 770 A h L^{-1}, which is a severe storage limitation for high-energy batteries when compared with the 3800 A h kg^{-1} for pure lithium. In addition, carbon intercalates lithium at just 0.2 volts *versus* lithium, so any slight overpotential such as could occur on fast recharging, could cause the formation of lithium dendrites[2] as shown in Fig. 2, due to the slow intercalation of the lithium into the carbon. These dendrites can penetrate the separator and short the cell. Thus, there is a desire for a material that has a slightly larger safety margin, say 0.5 volts. Some nano-sized oxides such as the spinel $Li_4Mn_5O_{12}$, which have a potential of 1.5 volts, are being considered where safety at high rates, not energy storage, is the all-critical concern.

Fig. 2 Dendritic growth of lithium during its electrodeposition. Reprinted with permission from R. R. Chianelli, *J. Cryst. Growth*, 1976, **34**, 239–244. Copyright 1976 Elsevier.

Many elements, such as aluminium, tin and silicon readily react with lithium at room temperature to form alloys like LiAl, $Li_{4.4}Sn$ and Li_4Si respectively, and have more than double the volumetric energy density of carbon. However, although these materials do react reversibly there is a very large volume change on reaction, 200 to 400% for the three materials discussed above. This results in rapid loss of capacity, as the SEI layer discussed cannot be cohesive and must be reformed each charge cycle resulting in a continuous build-up of this resistive material.

The Sn–Co story

Simple tin foil, which has an initial grain size of around 400 nm according to X-ray line broadening studies, reacts very readily with lithium and shows a high capacity for around 12 cycles, then the capacity falls rapidly due to the resistive build-up described above.[3] The grain size also drops to about 60 nm after 10 cycles, so in this case simply going nano does not work because the surface is too reactive. A break-through occurred in 2005, when SONY announced the commercialization of a tin anode, which was also reported to contain some cobalt and carbon.[4] This material has now been shown[5] to be a very clever nanostructure of nanosized Sn–Co nanoparticles embedded in a carbon matrix, as indicated in Fig. 3. The amorphous tin cobalt material has approximately the same local bonding structure as the alloy SnCo, but little long-range order showing no X-ray diffraction peaks except for graphitic carbon. The individual metal particles are around 5 nm in size. The overall size of the nanostructured particles is of the order of a micron, and it is likely that the protective SEI layer surrounds the overall particle not each intermetallic grain. The expansion of the tin, when it reacts with the lithium, is taken up by the soft carbon lattice without crumbling or growth of the tin-containing metallic reactant. The SEI layer therefore does not break down and need not be rebuilt on each cycle. The anode nanostructure also contains titanium, whose presence is critical to the stability of the electrode, but whose actual role has not been disclosed yet.

The amorphous tin–cobalt alloy has, as shown in Fig. 3, an almost continuous discharge/charge curve suggestive of a single phase reaction, unlike crystalline tin which shows the formation of several phases on both lithium insertion and removal. The capacity of the amorphous material remains constant, unlike bulk crystalline Sn–Co alloys which lose more than 50% of their capacity after 3 cycles.

Although this is an intriguing new material, it uses an essentially equimolar amount of cobalt added to the active tin component. Cobalt is too expensive and not sufficient in natural abundance to provide an anode for a large electric vehicle market. Thus, it must be replaced and Dahn's group set-out to understand why the Sn–Co composition works, and what the optimum Sn–Co–C composition is.[6] They studied a series of metal–cobalt compositions,[7] using a combinatorial approach with a sputtering synthesis method, and found that only Ti, V, Cr and Co made an amorphous phase with tin. As a critical aspect of these materials is that they be embedded in a carbon matrix, it is important that the alloying metal not react with the carbon. Of the metals that form an amorphous Sn–M compound, only cobalt was found not to form a stable carbide.[8] This is shown schematically in Fig. 4.

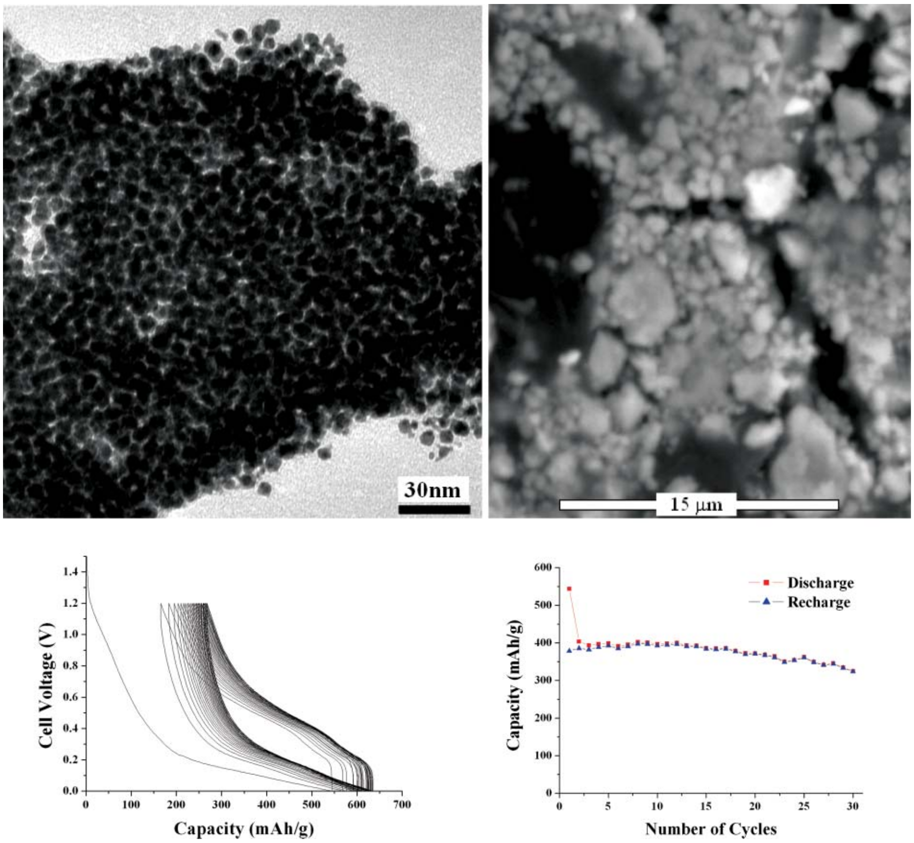

Fig. 3 (Top left) TEM image of Sn–Co–C–Ti anode showing the 5 nm metal particles embedded in carbon, and (right) SEM of overall micron size nanostructure. (Bottom) Cycling curve of the Sn–Co–C–Ti anode and its retention of capacity on cycling. Reprinted with permission from Q. Fan, P. Chupas and M. S. Whittingham, *Electrochem. Solid-State Lett.*, 2007, **10**, A274–A278. Copyright 2007 The Electrochemical Society.

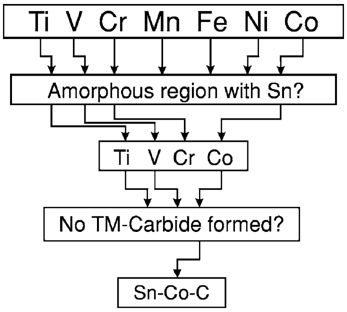

Fig. 4 Dahn model showing the two criteria for formation of an amorphous phase with tin, and lack of reactivity with carbon resulting in the choice of the Sn–Co–C composition as the amorphous anode. Reprinted with permission from A. D. W. Todd, R. E. Mar and J. R. Dahn, *J. Electrochem. Soc.*, 2007, **153**, A597–A604. Copyright 2007 The Electrochemical Society.

Why not silicon?

Silicon has by far the highest gravimetric energy density, 4.2 A h g^{-1}, of any lithium alloy, when forming Li_4Si. However, combined with the very large volume change on reaction with lithium, its much greater reactivity with for example oxygen than tin has prevented its commercial use to date. However, the incentive to use these materials is so great that a scientific breakthrough must be made. Metals such as tin and silicon can be grown in a variety of nanoforms. As noted for the tin–cobalt compound above when the small particles are small enough the structure can apparently take up the lithium without physical destruction of the structure. Fig. 5 shows schematically three different scenarios.[9] Thin films, like the tin foil discussed above, will eventually crumble on extended cycling. Micron-size particles are expected to break into smaller particles with concurrent loss of electrical contact between them and subsequent loss of electrochemical reactivity.

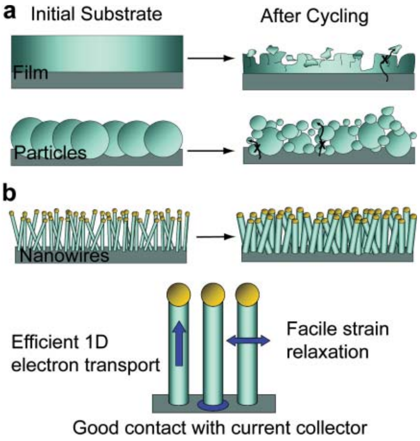

Fig. 5 Schematic of three morphologies for a potential anode: film, particles and fibers. Reprinted with permission from C. K. Chan, H. Peng, G. Liu, K. Mcilwrath, X. F. Zhang, R. A. Huggins and Y. Cu, *Nat. Nanotechnol.*, 2008, **3**, 31–35. Copyright 2008 Nature (London).

Recently, there have been several reports of the use of nanofibers. One of these, by Cui *et al.*,[9] investigated silicon nanofibers which are also depicted in Fig. 5. The goal in this case is to anchor the conducting silicon nanofibers to a substrate, which acts as the current collector. The fibers can expand parallel to the substrate and if small enough might not crumble. Using this morphology, the full capacity of silicon was obtained in the first cycle, and after a first cycle loss the capacity was quite stable over 10 cycles at about 3 A h g^{-1}, 75% of full capacity. This first cycle loss, in this case over 1 A h g^{-1}, is quite common but must be removed for a viable cell. The challenge will be to maintain the capacity over the desired several thousand cycles, without for example losing electrical contact with the substrate. Moreover, the volumetric capacity of any fiber structure is likely to be limited.

These fiber studies give another clue that materials like tin and silicon might well be able to replace carbon as the anode of choice for high energy and power batteries. However, a higher packing density will be needed and effort needs to be targeted at realistic morphologies. Perhaps a hybrid of such fibers and the SONY Sn–Co ideas will be effective. Our initial studies of a Si–Co–C anode show stable cycling at over 550 mA h g^{-1} for more than 12 cycles, after an irreversible loss of 180 mA h g^{-1} on the first cycle.

Oxide anodes

A number of transition metal oxides have been proposed as anodes including the spinel $Li_4Ti_5O_{12}$,[10] which reacts by an intercalation mechanism, at a potential of around 1.5 volts *vs* lithium metal. When in a nano form it reacts extremely fast and is being considered as the anode for power batteries when it would be coupled with a manganese oxide spinel, $LiMn_2O_4$ or with the nano $LiFePO_4$ to give a 2.0 to 2.5 volt battery that is very safe, not containing any reactive lithium metal. Different forms of titanium oxides are also of interest as they may be formed in a variety of nano morphologies, such as nanowires and nanotubes of TiO_2.[11–14] All of these titanium oxide compounds throw away around 1.5 volts of storable energy, so there is much interest in other nanosystems that might show high rates but which are around 0.5 volts *vs* lithium metal. One class of such materials that have received very little study are the hydrogen storage materials, which might be expected also to store lithium. One study[15] suggests that a $Ti_{46}Ni_{45}Nb_9$ alloy will intercalate lithium, but the capacity was low. Using a nano form of the alloy might be expected to give greater reactivity and initial results in our lab indicate that a preconditioning crumbling using hydrogen indeed allows for a greater lithium incorporation in a bcc titanium alloy.

Nanoparticles of some non-intercalating simple oxides such as MO (where M is Co, Ni, Cu or Fe)[16,17] show capacities of around 700 mA h g^{-1}, with nearly 100% capacity retention for up to 100 cycles. The synthetic method and particle size/morphology of oxides plays a critical role in their electrochemical activity, and it will be essential to determine the optimum morphology for reaction. We have studied[18] fibers of manganese oxide formed by electrospinning of non-aqueous solutions. These nanofibers, shown in Fig. 6, maintain their morphology although broken into shorter lengths after removal of the organic polymer. They show remarkable reversibility for a system that is believed to undergo structural change during reaction, maintaining a gravimetric capacity greater than that of carbon for over 50 cycles. However, their sloping voltage profile on lithium removal (*i.e.* on discharging of a battery) will create some engineering challenges in use. The reversibility of this system as well as of the simple CoO gives us encouragement that nano-materials will allow the use of structural change reactions for advanced batteries.

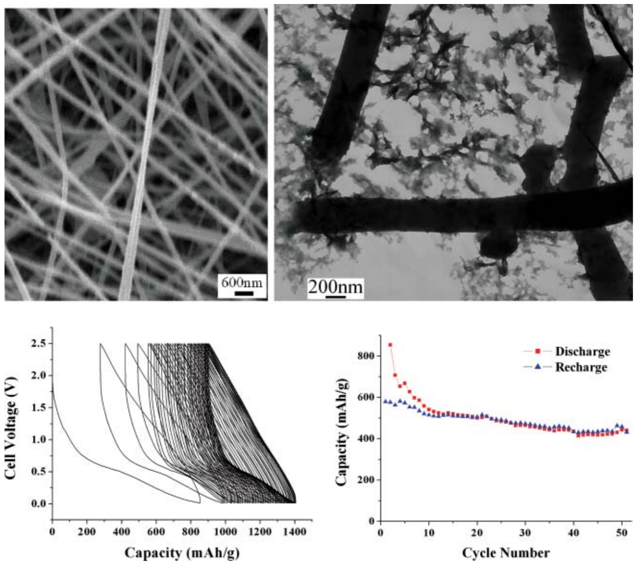

Fig. 6 (top) Electrospun fibers of MnO_x as formed, and after heating in oxygen at 300 °C, and (bottom) electrochemical insertion and removal of lithium, and the capacity on cycling. Reprinted with permission from Q. Fan and M. S. Whittingham, *Electrochem. Solid-State Lett.*, 2007, **10**, A48–A51. Copyright 2007 The Electrochemical Society.

The electrolyte and the solid electrolyte interphase layer (SEI)

In the manganese oxide described above the initial reaction with lithium exceeded by more than double the theoretical capacity of 940 mA h g^{-1} expected for the formation of Li_2O and manganese. This is due to the highly active manganese surface, which appears to catalyze the electrochemical decomposition of the electrolyte. The electrolyte salt used, $LiPF_6$, did not provide an effective surface protection layer. The formation of these SEI layers is especially critical for nanomaterials with their large and active surfaces. Over the last decade, there have been extensive searches for electrolyte salts that are lower cost and that do not generate HF in the presence of traces of moisture. One such salt is LiBOB, where the anion contains a boron tetrahedrally coordinated by two oxalate groups.[19–21] The lithium salt presents some synthetic challenges, because in the anhydrous state the lithium is five coordinate,[22] an unstable configuration; thus, it will grab any solvent molecule available to complete its coordination shell.[23]

However, LiBOB is an effective SEI former and in the case of the above manganese oxide anode successfully killed the over capacity as shown in Fig. 7.[24] If used as an additive at <10 mol% with >90% $LiPF_6$, the overall capacity on cycling was not diminished. At higher concentrations, the capacity was significantly impacted because the SEI layer was too thick and therefore highly resistive. The particular SEI additive used must be tailored to the particular nanomaterial used. Other boron salts

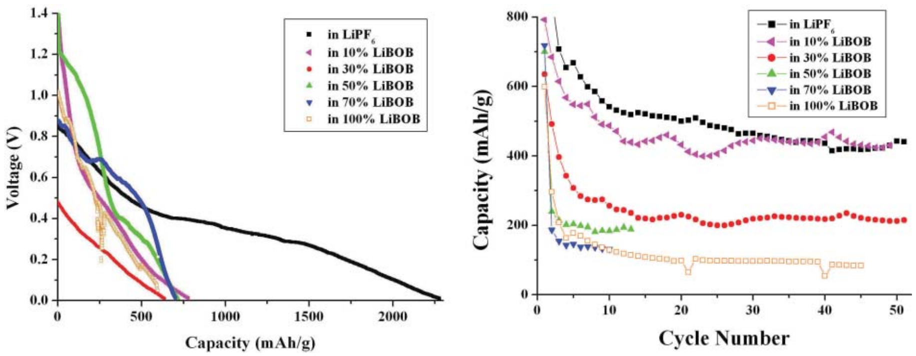

Fig. 7 Electrochemical behavior of electrospun manganese oxide nanofibers in LiBOB/$LiPF_6$ mixed electrolyte, all at 0.5 mA cm^{-2}. (Left) first discharge capacity in 1.0 M $LiPF_6$/EC(ethylene carbonate)/DMC(dimethyl carbonate) and mixed LiBOB salts showing the elimination of the excess capacity by LiBOB, and (right) discharge capacities as a function of cycle number.

are being actively studied, including more stable compounds such as Li–boron–difluoroxalate.

The formation of nano-thick films is not only important for the formation of SEI layers on the anode. The effective use of highly resistive cathodes, such as $LiFePO_4$, depends on the application of a conductive thin film on the surface.[25] Thin surface coatings have also been found effective in stabilizing the surfaces of cathodes such as those of the spinel $LiMn_2O_4$, and layered oxides.[26]

The cathode

One material that can be effectively used as very small particles down to the nano-size is $LiFePO_4$ because its reactivity is extremely selective. Only lithium comes in and out of the structure; the phosphate group is totally unreactive, so that there is no chance of reaction of the oxygen with the electrolyte. Even on reaction with excess lithium the phosphate group remains intact as Li_3PO_4 and Fe metal are formed. Thus, this material is an excellent candidate for increasing the rate capability by reducing the particle size, which can be done mechanically or by solvothermal synthesis.[27]

The lithium iron phosphate/iron phosphate reaction[28] in micron and larger sizes is a two phase system with very low solubility at the extremes $Li_{1-y}FePO_4$ and $Li_\delta FePO_4$, where y and δ are $<<1\%$. However, as the particle size decreases, so y and δ increase so that for 100 nm particles, $y = 3.2\%$ and $\delta = 2.8\%$.[29] The unit cell volume also decreases slightly as the particle size decreases;[27] this has also been reported in other systems.[30] It is postulated that if the particle size is sufficiently small then Li_xFePO_4 would be single phase for all values of x at room temperature, just as is observed at temperatures over 400 °C.[31] This results in a change in the reaction mechanism, where in large particles at room temperature a reaction front moves through the crystallites in the a direction, whilst the lithium moves in/out of the tunnels "tunnel by tunnel" in the b direction.[32] There is believed to be an amorphous nano-region at the interface between the $LiFePO_4$ and $FePO_4$ phases. However, for nanosized material the lithium will diffuse in/out of each tunnel progressively.

A challenge to the use of $LiFePO_4$ in electrochemical devices is its very poor electronic conductivity, particularly in very pure material where there are no impurities. $LiFePO_4$ synthesized using reagent grade materials, particularly when using carbon-containing reactants has an electronic conductivity of 10^{-6}–10^{-8} S cm^{-1}. The conductivity must therefore be enhanced by mixing in carbon, or specifically by forming a conductive layer on the surface normally using carbon. However, the smaller the particle size the larger the proportion of the system taken up by the conductive coating. Thus, there is a lower practical limit to the size of electroactive $LiFePO_4$ that can be used in practical batteries. Another issue with using small particles, particularly nano, is the packing density (also known as the tap density), which drops dramatically as the particle size decreases approaching 1 g cm^{-3}. This substantially reduces the volumetric energy density. So nano is not the total panacea. There is an optimum particle size, which has not yet been determined.

The amount of carbon additive or carbon coating can be reduced if a highly conductive network is incorporated into the structure. One approach is to include such a material, like carbon nanotubes, into the synthesis reactor as done hydrothermally.[33] The resulting $LiFePO_4$ was found to cycle very well, as shown in Fig. 8. Less than 1% carbon nanotubes, because of their extreme aspect ratio, attains the percolation threshold for electron conductivity.

It is clear now that going nano-size is effective for the olivine class of material, $LiMPO_4$, not only for $LiFePO_4$ but also for $LiMnPO_4$. The latter does not readily release its lithium in bulk size, probably because the lattice mismatch between $LiMnPO_4$ and $MnPO_4$ is much greater, 10%, than that for $LiFePO_4$/$FePO_4$. In addition, the Jahn–Teller distortion associated with Mn^{3+} is also likely to hinder the lithium intercalation. Fig. 9 compares the rate capability of 40 nm $LiFePO_4$[34] and 140 nm $LiMnPO_4$[35] synthesized using solvothermal reactions. It is to be expected that 40 nm $LiMnPO_4$ might show superior performance, as well as perhaps some nonstoichiometric behavior, Li_xMnPO_4.

Another set of interesting nano-materials is exemplified by the vanadium oxides, which can be readily formed in a range of morphologies, and have been proposed for use in both batteries and pseudocapacitors. Fig. 10 shows three fibrous morphologies of vanadium pentoxide, and the marked impact on the power/energy curve in lithium cells.[36]

Fig. 11 shows SEMs of several other morphologies of vanadium oxides,[37,38] emphasizing the opportunities available with vanadium; apart from the example described above no systematic

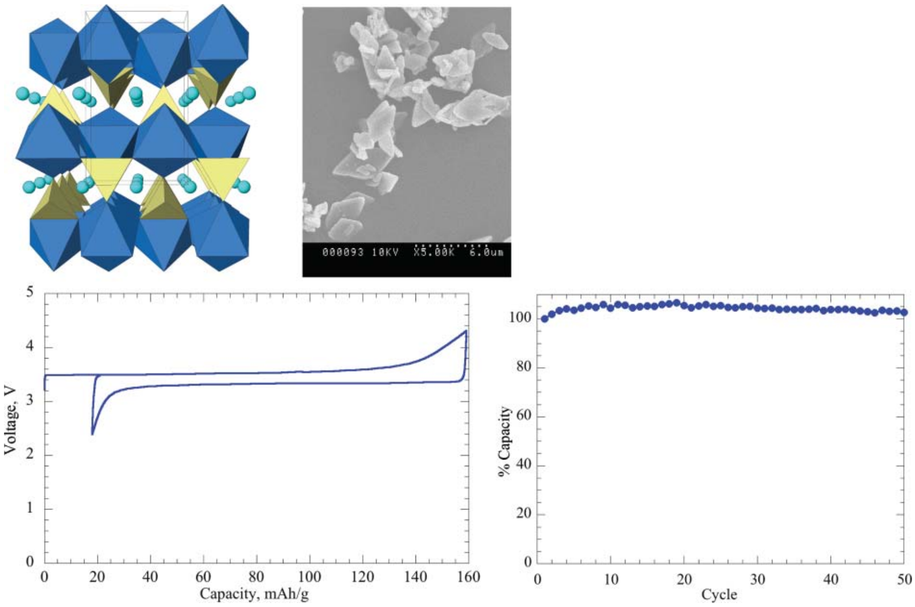

Fig. 8 (Top left) structure and (top right) morphology of $LiFePO_4$. The diffusion direction, *b*, is perpendicular to the plates, *i.e.*, in the thin direction (these crystals with an aspect ratio of around 10 have a surface area of 7 m^2 g^{-1}). (Bottom left) discharge curve of $LiFePO_4$, and (bottom right) capacity retention of $LiFePO_4$ using hydrothermal material and carbon nanotubes. Reprinted with permission from J. Chen and M. S. Whittingham, *Electrochem. Commun.*, 2006, **8**, 855–858. Copyright 2006 Elsevier.

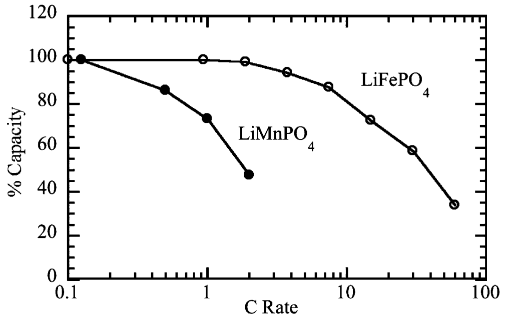

Fig. 9 Rate capability of the two olivines, $LiFePO_4$ and $LiMnPO_4$. Capacity as % of the C/10 capacity.

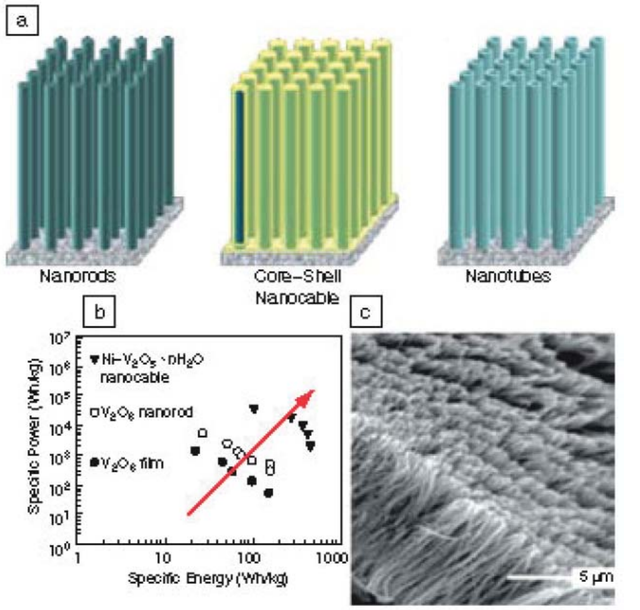

Fig. 10 Variation of the storage and rate capability of vanadium oxide as a function of its morphology. Published by permission from Y. Wang, K. Takahashi, K.H. Lee and G.Z. Cao, *Adv. Funct. Mater.*, 2006, **16**, 1133–1144. Copyright 2006 Wiley-VCH.

study has been undertaken to determine the role of morphology on the electrochemical behavior. Many of these materials were synthesized hydrothermally, a technique that leads to very uniform particle sizes and often spherical particles of nanosized crystallites,[39] as indicated in Fig. 11. The hydrothermal process is now being commercialized for the manufacture of submicron $LiFePO_4$. Antonietti *et al.* have also recently discussed[40] the opportunities offered by related oxides such as those of molybdenum and tungsten.

Conclusions and challenges facing nanomaterials

Nanomaterials have a key role to play in the next generation of batteries. However, not all materials are appropriate to use at the nano-level, just those that undergo the desired reaction in a highly selective manner. It is likely that nanomaterials will be built into smart nanostructures, which again will enhance the selectivity of the desired reaction, such as is found in the SONY tin–cobalt anode. The building of the nanostructured solid electrolyte interphase is critical to the long-term stability and operation of electrochemical cells. Cathodes with non-reactive anionic groups are prime candidates for use at the nano-level, but there is a limit to "nano" as the packing density decreases as the particle size decreases.

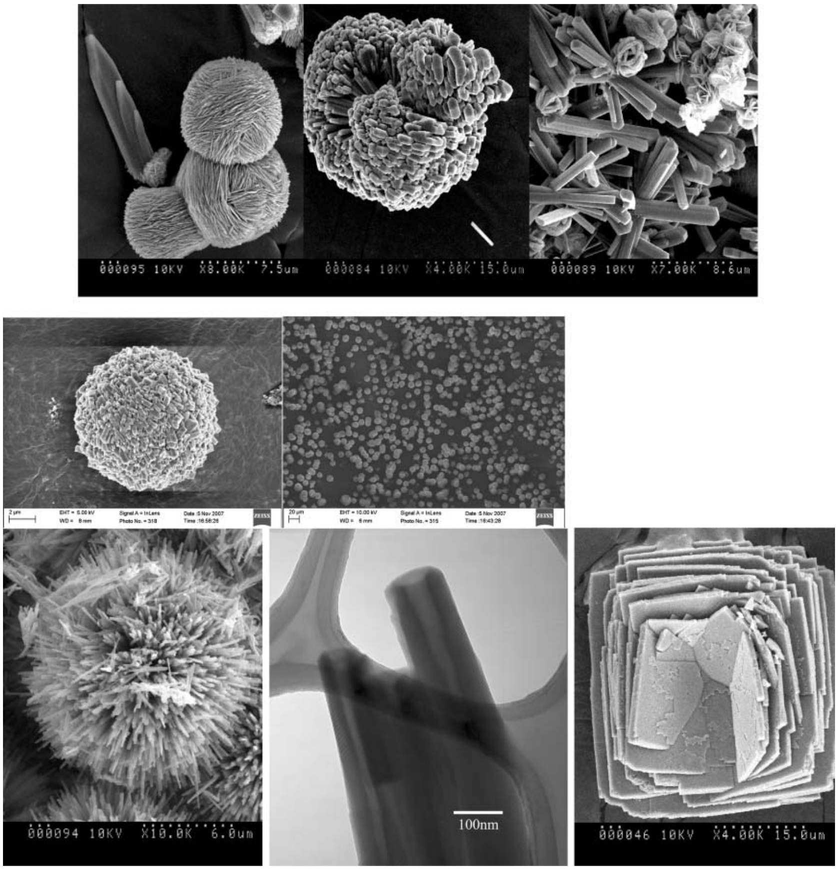

Fig. 11 Some vanadium oxide and phosphate morphologies. Top: lithium vanadium oxides; middle: lithium vanadyl phosphate, showing the sphere made up of nanocrystals, and the uniformity of spheres made by the hydrothermal process; bottom: some vanadium oxide nanotubes morphologies, nano-urchins, nanotubes and the precursor plates.

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